

# Emissions from forest fires near Mexico City

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## Abstract

The emissions of  $\text{NO}_x$  and HCN (per unit amount of fuel burned) from fires in the pine-savannas that dominate the mountains surrounding Mexico City (MC) are about 2 times higher than normally observed for forest burning. The  $\text{NH}_3$  emissions are about average for forest burning. The  $\text{NO}_x/\text{VOC}$  mass ratio for the MC-area mountain fires was  $\sim 0.38$ , which is similar to the  $\text{NO}_x/\text{VOC}$  ratio in the MC urban area emissions inventory of 0.43, but much larger than the  $\text{NO}_x/\text{VOC}$  ratio for tropical forest fires in Brazil ( $\sim 0.068$ ). The nitrogen enrichment in the fire emissions may be due to deposition of nitrogen-containing pollutants in the outflow from the MC urban area. This effect may occur worldwide wherever biomass burning coexists with large urban areas (e.g. the tropics, southeastern US, Los Angeles Basin). The molar emission ratio  $\text{HCN}/\text{CO}$  for the mountain fires was  $\sim 0.0128 \pm 0.0096$ : 2–9 times higher than widely used literature values for biomass burning. The MC-area/downwind molar ratio of  $\text{HCN}/\text{CO}$  is about  $0.003 \pm 0.0003$ . Thus, if other types of biomass burning are relatively insignificant, the mountain fires may be contributing about 23% of the CO production in the MC-area ( $\sim 98$ – $100^\circ\text{W}$  and  $19$ – $20^\circ\text{N}$ ). Comparing the  $\text{PM}_{10}/\text{CO}$  mass ratio in the MC Metropolitan Area emission inventory (0.011) to the  $\text{PM}_1/\text{CO}$  mass ratio for the mountain fires (0.133) then suggests that these fires could produce as much as  $\sim 78\%$  of the fine particle mass generated in the MC-area.

## 1 Introduction

A main objective of the March 2006 MILAGRO campaign is to understand the chemical evolution and influence of the Mexico City (MC) area plume on the regional to global scale. In a typical MC plume, a long-range transport event begins when the boundary layer over MC increases to a depth sufficient for pollutants to escape the confines of the mountains that surround MC – usually between the hours of 10:00 a.m. and 06:00 p.m. During the January through June dry season, readily visible biomass burn-

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ing in the surrounding mountains also occurs mainly during the afternoon. Thus, an air mass may mix with: fire emissions upwind of MC, then the MC pollutants (which may contain some urban biomass burning emissions), and then fire emissions immediately downwind of MC. The resulting plume then further evolves chemically downwind during regional transport. A key goal of MILAGRO is to develop photochemical models that accurately reproduce the actual evolution of the MC plume measured during March 2006 research flights. For these dry season measurements, entrained fire emissions could affect the observed photochemical transformations. Since HCN is likely emitted mostly or exclusively by fires, measurements of HCN emissions by fires and of HCN in the downwind plume could help quantify the biomass-burning contribution to the downwind plume.

As part of MILAGRO, an instrumented US Forest Service Twin Otter aircraft measured the emissions from 63 fires throughout south-central Mexico. This paper focuses on a “study area” ranging from 19–20 N and 98–100 W that includes the MC metropolitan area and the adjacent mountains. This “box” approximates the footprint relevant for airborne measurements several hours to several days downwind of MC. The Twin Otter sampled 8 fires in this study area, of which 7 were sampled with instrumentation capable of measuring reactive nitrogen species. All the fires were located in the pine-savanna vegetation type that dominates the mountains near MC. One plume from a similar MC-area fire was profiled by the NCAR C-130 while measuring HCN and CO and both these species were also measured regionally on board the C-130. The purpose of this paper is to present emission factor and emission ratio measurements for the MC-area pine forest fires and a few preliminary implications of those measurements. In addition, we propose that the emissions from these fires were probably impacted by the deposition of urban pollutants in the MC plume. This is likely relevant to understanding atmospheric chemistry wherever biomass burning coexists with urban areas globally. Separate papers will present other atmospheric chemistry measurements made on the MILAGRO research aircraft and the emission factors for the other fires sampled throughout south-central Mexico. The latter included tropical

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deforestation fires, other forest fires, shrub and grassland fires, and agricultural waste burning.

## 2 Experimental details

### 2.1 Data acquisition

#### 5 2.1.1 Airborne FTIR (AFTIR)

An airborne Fourier transform infrared spectrometer (AFTIR) on the Twin Otter provided the measurements of several nitrogen species and other reactive and stable trace gases present above ~5-20 ppbv. The AFTIR had a dedicated, halocarbon-wax, coated inlet that directed ram air through a Pyrex, multipass cell. The AFTIR was  
10 used for continuous measurements of water vapor ( $\text{H}_2\text{O}$ ), carbon dioxide ( $\text{CO}_2$ ), carbon monoxide ( $\text{CO}$ ), and methane ( $\text{CH}_4$ ); or to grab samples for signal averaging and measurement of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ , nitric oxide ( $\text{NO}$ ), nitrogen dioxide ( $\text{NO}_2$ ), ammonia ( $\text{NH}_3$ ), hydrogen cyanide ( $\text{HCN}$ ),  $\text{CH}_4$ , ethene ( $\text{C}_2\text{H}_4$ ), acetylene ( $\text{C}_2\text{H}_2$ ), formaldehyde ( $\text{HCHO}$ ), methanol ( $\text{CH}_3\text{OH}$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ), formic acid ( $\text{HCOOH}$ ), and  $\text{O}_3$ .  
15 The details and the accuracy of the AFTIR technique are described by Yokelson et al. (1999, 2003a, b).

#### 2.1.2 Whole air sampling (WAS)

A forward facing, 25 mm i.d. stainless steel elbow sampled ram air into stainless steel canisters on board the Twin Otter. Two-liter canisters were shipped to the University of  
20 Miami and analyzed by GC with a flame ionization detector (FID) for  $\text{CH}_4$ , and the following non-methane hydrocarbons: ethane,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ , propane, propene, isobutane, n-butane, t-2 butene, 1-butene, isobutene, c-2-butene, 1,3 butadiene, cyclopentane, isopentane, and n-pentane, with detection limits in the low pptv.  $\text{CO}$  was measured

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in parallel with the CH<sub>4</sub> measurement, but utilized GC with a Trace Analytical Reduction Gas Detector (RGD). Starting 18 March, 800-ml canisters were also filled with the same sampling system and analyzed later at the United States Forest Service (USFS) Fire Sciences Laboratory by GC/FID/RGD for CO<sub>2</sub>, CO, CH<sub>4</sub>, H<sub>2</sub>, and several C<sub>2</sub>-C<sub>3</sub> hydrocarbons. Details of the canister analysis are given by Weinheimer et al. (1998), Flocke et al. (1999), and Hao et al. (1996). GC/MSD measurements of higher molecular weight hydrocarbons and halocarbons will be reported elsewhere. CO and CH<sub>4</sub> were measured with high accuracy by both the AFTIR and the cans, which facilitated coupling the data from these instruments.

### 2.1.3 Nephelometry

The large-diameter, fast-flow, WAS inlet also supplied sample air for a Radiance Research Model 903 integrating nephelometer that measured  $b_{\text{scat}}$  at 530 nm at 0.5 Hz; synchronized with a Garmin GPS. Both were available and logged by USFS starting 18 March. Immediately after the field campaign, the measurements of  $b_{\text{scat}}$  by the nephelometer were compared to gravimetric (filter-based) measurements of the mass of particles with aerodynamic diameter <2.5 microns (PM2.5) for 14 fires in pine forest fuels burned in the USFS Missoula biomass fire simulation facility. We obtained (and applied) a linear relationship between  $b_{\text{scat}}$  and PM2.5 in  $\mu\text{g}/\text{m}^3$  of standard temperature and pressure air.

$$b_{\text{scat}} \times 228\,000(\pm 11\,000(2\sigma)) = \text{PM2.5}(\mu\text{g}/\text{m}^3) \quad (1)$$

The conversion factor is similar to the 250 000 measured by Nance et al. (1993) for smoke from Alaskan wildfires in coniferous fuels, which they showed was within  $\pm 20\%$  of the factors determined in other studies of biomass burning smoke. In addition, an earlier study in the Missoula fire lab, with fires in a larger variety of wildland fuels, found that the conversion factor of 250 000 reproduced gravimetric particle mass measurements within  $\pm 12\%$  (Trent et al., 2000).

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#### 2.1.4 TEM analysis and co-located, fast, isokinetic particle and CO<sub>2</sub> measurements

An isokinetic particle inlet (designed by Chuck Wilson of the University of Denver and built at NCAR) was used on the Twin Otter to sample fine particles with a diameter cut-off of a few microns. Both the measured and previously published particle size distributions show that particles of diameter below 1 micron account for nearly all the fine-particle (PM<sub>2.5</sub>) mass emitted by biomass fires (Radke et al., 1991). This inlet supplied sample air for two MPS-3 particle samplers (California Measurements, Inc.) that were used to collect 182 samples over time intervals of ~1 to 10 min for analyses using transmission electron microscopy (TEM). Each sampler consists of a three-stage impactor, which collects particles with aerodynamic diameters of >2, 2–0.3, <0.3 μm. A CM 200 (FEI) microscope was used for subsequent TEM analysis at Arizona State University, which revealed details of the chemistry and structure of individual particles.

The same inlet also supplied a LiCor (Model # 7000) measuring CO<sub>2</sub> and H<sub>2</sub>O at 5 Hz and the UHSAS (Ultra High Sensitivity Aerosol Sizer) (both deployed by U. Colorado). The UHSAS provided the number of particles in each of 99 user-selectable bins for diameters between 55 and 1000 nm at 1 Hz. All three inlets were located near each other as can be seen in the photo at (<https://www.umat.edu/chemistry/faculty/yokelson/galleries/Mexico/Airborne/Aircraft/index.html>). Use of a single inlet for both the UHSAS and fast CO<sub>2</sub> enabled coupling the particle and trace gas data.

#### 2.1.5 HCN and CO measurements on the C-130

The Caltech CIMS measured selected product ions on the C-130 via reaction of the reagent ion CF<sub>3</sub>O<sup>−</sup> with analytes directly in air. HCN is measured by monitoring the product ion with m/z=112, which is the cluster of CF<sub>3</sub>O<sup>−</sup> with HCN. The sensitivity is dependant on the water vapor mixing ratio. Sensitivity changes due to water vapor changes are corrected for using the dewpoint hygrometer water measurement from the C-130 aircraft, and a water calibration curve which has been generated though laboratory measurements. Non-water sensitivity changes are corrected for using in-

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flight standard addition calibrations of  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  (other species measured by the CIMS) and proxied to laboratory calibrations of HCN. The detection limit ( $\text{S/N}=1$ ) for HCN for a 0.5 s integration period is better than 15 pptv for moderate to low water vapor levels ( $\text{H}_2\text{O}$  mixing ratio  $\leq 0.004$ ) (Crounse et al., 2006). The NCAR/NSF C-130 CO vacuum UV resonance fluorescence instrument is similar to that of Gerbig et al. (1999). The MILAGRO data have a 3 ppbv precision, 1-second resolution, and a typical accuracy of  $\pm 10\%$  for a 100 ppbv ambient mixing ratio.

#### 2.1.6 Airborne sampling protocol

The Twin Otter and C-130 were based in Veracruz with the 4 other MILAGRO research aircraft (<http://mirage-mex.acd.ucar.edu/>). The Twin Otter flew 67 research hours from 4 March to 29 March in the approximate range 16–23 N and 88–102 W. Background air was thoroughly characterized while searching for fires. The nephelometer, LiCor, UHSAS, and the AFTIR were usually operated continuously in background air with similar time resolutions from 0.5 to 5 Hz. At many key locations, the MPS-3 obtained integrated samples and WAS and AFTIR acquired “grab” samples of background air. To measure the initial emissions from the fires, we sampled smoke less than several minutes old by penetrating the column of smoke 150–500 m above the flame front. The LiCor, UHSAS, and nephelometer profiled their species while penetrating the plume. The AFTIR, MPS-3, and WAS were used to acquire “grab” samples in the smoke plumes. More than a few kilometers downwind from the source, smoke samples are usually already “photochemically aged” and better for probing post-emission chemistry than estimating initial emissions (Goode et al., 2000; Hobbs et al., 2003). To determine excess concentrations in the smoke-plume grab-samples, paired background grab-samples were acquired just outside the plume.

The C-130 concentrated on sampling regional background air and the MC outflow up to several days old. However, one smoke plume was profiled near MC, while making pseudo-continuous measurements of HCN, CO, and other species. HCN and CO were also measured extensively throughout the region.

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## 2.1.7 Fire and fuel consumption measurements

One of the fires sampled with the Twin Otter was a planned fire that was part of a program implemented by CONAFOR (Mexican Federal Forest Service) and the Department of Ecology of the state of Morelos. Prescribed fires are conducted every year before the fire season to reduce fuels and wildfires in the region. However, CONAFOR agreed to burn one of the areas in early March to allow us to measure fire behavior, fuel consumption, and smoke emissions representative of the fire season. The fire was in the Corredor Biológico Chichinautzin, National Park, which has one of the highest incidences of forest fires in central Mexico. The fuel consumption was 6.54 Mg/ha – determined by the difference between pre- and post-fire fuel loading measured by the linear intersect method (Brown, 1974). The area burned by the fire was 22.2 ha. Similar area and fuel consumption measurements were made on the other fires that we sampled and additional fires that were not sampled by the Twin Otter (Table 1).

## 2.2 Data processing and synthesis

Grab samples or profiles of an emission source provide excess mixing ratios ( $\Delta X$ , the mixing ratio of species “X” in the plume minus the mixing ratio of “X” in the background air).  $\Delta X$  reflect the instantaneous dilution of the plume and the instrument response time. Thus, a useful, derived quantity is the normalized excess mixing ratio where  $\Delta X$  is compared to a simultaneously measured plume tracer such as  $\Delta \text{CO}$  or  $\Delta \text{CO}_2$ . A measurement of  $\Delta X/\Delta \text{CO}$  or  $\Delta X/\Delta \text{CO}_2$  made in a nascent plume (seconds to a few minutes old) is an emission ratio (ER). For any carbonaceous fuel, a set of ER to  $\text{CO}_2$  for the other major carbon emissions (i.e.  $\text{CO}$ ,  $\text{CH}_4$ , a suite of non-methane organic compounds (NMOC), particulate carbon, etc) can be used to calculate emission factors (EF, g compound emitted/kg dry fuel) for all the emissions quantified from the source using the carbon mass-balance method (Yokelson et al., 1996). In this project, the carbon data needed to calculate EF was provided mostly by AFTIR measurements of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and NMOC and also canister sampling of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and NMHC.

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The particle data allowed inclusion of particle carbon in the carbon mass balance. Next we summarize a few details of the methods we used to synthesize the data from the various instruments on the aircraft and to calculate ER and EF.

### 2.2.1 Estimation of fire-average, initial Emission Ratios (ER) for trace gases

5 First we describe the computation of ER on a molar basis to CO and/or CO<sub>2</sub> for each species detected in the AFTIR and canister grab samples. This is done for each individual fire or each group of co-located, similar fires. If there is only one grab sample of a fire (as for the 9 March fire) then the calculation is trivial and equivalent to the definition of  $\Delta X$  given above. For multiple grab samples of a fire (or group of similar  
10 fires) then the fire-average, initial ER were obtained from the slope of the least-squares line (with the intercept forced to zero) in a plot of one set of excess mixing ratios versus another. This method is justified in detail by Yokelson et al. (1999).

The ER to CO<sub>2</sub> for the NMHC detected in the U-Miami cans is derived by multiplying the can ER to CO times the AFTIR ER CO/CO<sub>2</sub>. The ER we obtained for each fire  
15 can be retrieved from the EF in Table 2 (calculated as described next) after accounting for any difference in molecular mass. The modified combustion efficiency (MCE,  $\Delta\text{CO}_2/(\Delta\text{CO}_2 + \Delta\text{CO})$ ) for each fire is also shown in Table 2. The MCE indicates the relative amount of flaming and smoldering combustion for biomass burning. Lower MCE indicates more smoldering (Ward and Radke, 1993).

20 The HCN/CO ratio for the study region and downwind measurements is the average ratio for all the C-130 measurements in the urban area or outflow, but that were not in distinct plumes. The  $\Delta\text{HCN}/\Delta\text{CO}$  emission ratio for the fire plume sampled by the C-130 was the integrated excess HCN divided by the integrated excess CO.

### 2.2.2 Estimation of fire-average, initial Emission Factors (EF)

25 We estimated fire-average, initial EF for PM<sub>1</sub> and each observed trace gas from our fire-average, initial ERs using the carbon mass balance method (Yokelson et al., 1999).

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In brief, we assume that all the volatilized carbon is detected and that the fuel carbon content is known. By ignoring unmeasured gases, we may inflate the emission factors by 1–2% (Andreae and Merlet, 2001). We assumed that all the fires burned in fuels containing 50% carbon by mass (Susott et al., 1996), but the actual fuel carbon percentage may vary by  $\pm 10\%$  ( $2\sigma$ ) of our nominal value. (EF scale linearly with assumed fuel carbon percentage.) The fire-average, initial EF for each compound and fire are listed in Table 2. Because NO is quickly converted to NO<sub>2</sub> after emission, we also report a single EF for “NO<sub>x</sub> as NO.”

### 2.2.3 Determination of particle mass

The nephelometer was used to profile the mass to volume ratio for PM<sub>2.5</sub> during plume penetrations of the 18 March fire. The simultaneously recorded CO<sub>2</sub> data allowed determination of the mass ratio for PM<sub>2.5</sub> to CO<sub>2</sub> for each pass through the plume. The ER (on a mass basis) for PM<sub>2.5</sub> to CO<sub>2</sub> for each fire (or group of similar fires) was obtained by linear regression as above, except that the integrated excess mass values for each profile through the plume were used in lieu of grab sample excess mixing ratios. Assuming the particles were 60% carbon by mass (Ferek et al., 1998) gave the contribution of PM<sub>2.5</sub> to the total carbon emitted for the emission factor calculations. The PM<sub>2.5</sub>/CO<sub>2</sub> mass ratio times EFCO<sub>2</sub> (g/kg) gave EFPM<sub>2.5</sub> (g/kg). The EFPM<sub>2.5</sub> for 18 March is likely accurate to within  $\pm 10\%$ .

Because, the nephelometer was not available before 18 March, the UHSAS particle size data which was collected at a sample rate similar to that of the nephelometer (and from a nearby inlet that was also used for fast CO<sub>2</sub> measurements) was used to determine particle mass as described next.

We assumed spherical particles and integrated over the size distribution measured by the UHSAS, to obtain an estimate of the volume of particles at 1 Hz. For each of the 8 plume penetrations on 18 March that featured both the UHSAS and nephelometer sampling pine-forest fires in the MC-area mountains, the integrated particle mass was ratioed to the integrated particle volume. For the densest plumes, only data from

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the more dilute parts of the plume were used to avoid effects of saturation in the UH-SAS. The mass to volume ratio was  $1.858 \pm 0.183$  g/cc. It is tempting to interpret this mass/volume ratio as an estimate of particle density, but the real density should be lower since: the particles are not perfectly spherical, there is a small amount of particle mass in the diameter range 1–2.5 microns, and the particles are also ~8% black carbon by mass (Ferek et al., 1998), which would partially absorb the UHSAS laser. In any case, we used the above “empirical” m/v ratio to convert the integrated UHSAS particle volume to integrated particle mass for the pine forest fire, plume-penetration samples obtained 6–17 March. The simultaneous co-located CO<sub>2</sub> measurements again provided the comparable integrated mass of CO<sub>2</sub> for each plume penetration. The ER (on a mass basis) for PM<sub>1</sub> to CO<sub>2</sub> were used as described above for the emission factor calculations. The EFPM<sub>1</sub> values obtained as described above, may only be accurate to  $\pm 25\%$ , but are not large enough to introduce significant error in the trace gas EF. Because of the size distribution mentioned above, EFPM<sub>1</sub> should be essentially equivalent to EFPM<sub>2.5</sub>.

### 3 Results and discussion

#### 3.1 Description and relevance of fires sampled

Detailed information about the MODIS and AVHRR hotspots detected in the entire country of Mexico since 2003 is conveniently tabulated at ([http://www.conabio.gob.mx/conocimiento/puntos\\_calor/doctos/puntos\\_calor.html](http://www.conabio.gob.mx/conocimiento/puntos_calor/doctos/puntos_calor.html)). The data shows that fire activity increases gradually and then sharply from November to May before dropping to low levels by August. The months of March, April, and May accounted for about 12, 31, and 43% of the total MODIS hotspots from 2003–2006, respectively. Nationwide, March 2006 showed average activity for March not counting the 2003 El Niño year. However, Mexican Forestry personnel (personal communication to E. Alvarado) and casual inspection of MODIS hotspot maps produced by the University of Maryland (UMD) Web

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Fire Mapper (<http://maps.geog.umd.edu>) (Justice et al., 2002) indicate that the level of fire activity in March 2006 in the mountains around MC was above normal for March in that area and similar to levels that normally occur in that area in April.

Table 1 shows location, time, and any fuel consumption and area information we have for the pine-forest fires that we were able to sample in the study area. Figure 1 shows all the MODIS UMD hotspots detected during March 2006 from 98–100 W and 19–20 N – the geographic limits of our MC-area study. Fire detections were made in the study area on 19 of the 31 days in March and totaled 218. The true number of fires is much larger as discussed below. Clouds or lack of coverage likely impacted the hotspot count on at least 14 of 31 days and that combined with a possible lack of sufficiently large fires at overpass time likely explain the days without detections. None of the fires that we sampled from the air in the study area registered as UMD-MODIS hotspots, because they were mostly short-lived (~1 h) and occurred >1 h before or after the Terra or Aqua overpass. However our fires were located in the precise areas showing the most hotspot activity. Thus, we conclude that (1) the number of hotspots provides a lower limit on the number of fires, (2) the hotspots are concentrated in the areas with the most burning, and (3) the fires we sampled were in the areas with the most burning.

Figure 2 is a photo, taken a few km NW of the site of fire 3.6\_4, at 05:13 p.m. LT on 6 March. Well after the last daytime satellite overpass at 02:20 p.m., a large number of pine-forest fires are burning in, and mixing with, the MC outflow on a mountain pass to the south of the city.

### 3.2 Initial emissions from pine-forest fires in MC-area mountains

Table 2 gives the EF for every species we detected for each fire (or group of similar fires) and the average and standard deviation for all the species measured. The standard deviation is a fairly large percentage of the average value for many species. Figure 3 shows EFPM1 vs MCE (index of the relative amount of flaming and smoldering). Figure 3 suggests that much of the variability in EFPM1 is correlated with the

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different relative amounts of flaming and smoldering that occur naturally on biomass fires. For nitrogen species there is also a contribution to variability from the differing fuel nitrogen content (Yokelson et al., 1996, 2003a). The sum of the EF for VOC in Table 2 is 18.85 g/kg. However, oxygenated VOC (OVOC) normally dominate the NMOC emitted by biomass fires and we did not have the capability to detect several OVOC common in biomass smoke (Christian et al., 2003) in this study, so we use 20 g/kg as a conservative estimate of the real sum of VOC, which may be as high as 25 g/kg.

### 3.3 Comparison to other biomass burning emission factors and the influence of urban pollution on fire emissions

Most of the average EF shown in Table 2 are similar to previously measured average values for forest burning. For instance, our study average EFPM1 ( $11 \pm 6$  g/kg) agrees well with the recommended EFPM2.5 for extratropical forest burning ( $13 \pm 7$  g/kg) in Andreae and Merlet (2001). However, large differences with previous forest fire measurements occur for  $\text{NO}_x$  and HCN. In Fig. 4 we compare our EF for  $\text{NO}_x$ , HCN, and  $\text{NH}_3$ , to those from other types of biomass burning. In Fig. 4 the data for MC-area pine forest is from the present study. The data for US pine forest is an average from several published sources (Yokelson et al., 1996; Goode et al., 1999; Radke et al., 1991) and also includes some very similar unpublished lab-fire values obtained during the following studies (Christian et al., 2003; Christian et al., 2007<sup>1</sup>). The Brazil tropical forest values are from a 2004 field campaign in the Amazon (Yokelson et al., 2007<sup>2</sup>) and the African savanna data are from (Yokelson et al., 2003a). The recommendations

<sup>1</sup>Christian, T. J., Karl, T. G., Yokelson, R. J., Guenther, A., and Hao, W. M.: The tropical forest and fire emissions experiment: Comprehensive laboratory measurements of the emissions from burning sugar cane and other tropical fuels, Atmos. Chem. Phys. Discuss., in preparation, 2007.

<sup>2</sup>Yokelson, R. J., Karl, T., Artaxo, P., Blake, D. R., Christian, T. J., Griffith, D. W. T., Guenther, A., and Hao, W. M.: The tropical forest and fire emissions experiment: Overview and airborne fire emission factor measurements, Atmos. Chem. Phys. Discuss., submitted, 2007.

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of Andreae and Merlet (2001) for extratropical forest are also shown.

For  $\text{NH}_3$  the MC-area pine forest EF is close to what has been measured for other forest burning and the recommendation of Andreae and Merlet. However for  $\text{NO}_x$  the MC-area pine forest EF is about 4 times typical measurements for other forests and more than twice the recommendation of Andreae and Merlet. For HCN the MC-area pine forest fire EF is about 3 times that measured for US pine forests and about twice that for tropical forests and savannas. Our EF HCN is almost 7 times higher than the recommendation of Andreae and Merlet. The higher values for HCN could also indicate that a larger EF for acetonitrile ( $\text{CH}_3\text{CN}$ ) is appropriate, but we did not measure the latter.

It is interesting that our average EF for  $\text{NO}_x$  and HCN are 3–4 times the average measured for US pine forests. The difference in the mean is statistically significant for  $\text{NO}_x$  ( $7.44 \pm 3.0$  MC-area,  $1.71 \pm 1.7$  US), whereas for HCN the variability in the MC-area EF overlaps the US mean ( $1.023 \pm 0.66$  MC-area,  $0.39 \pm 0.24$  US). Nevertheless, the indication is that the true HCN mean is also higher for the MC-area. We note that the MC-area forests are heavily impacted by deposition of MC pollutants (Fenn et al., 1999), whereas the US pine forest data is from pristine pine forest ecosystems. Thus we speculate that the high  $\text{NO}_x$  and HCN emissions in the MC-area pine forests may be due to enrichment of fuel nitrogen components that contribute to the emissions of these species via deposition of nitrogen-containing pollutants to the vegetation. The near-normal  $\text{NH}_3$  emissions may indicate that they arise from other more ubiquitous fuel nitrogen components. These assumptions could be further tested in the future after we analyze the IR spectra from the pine forest fires sampled in less-polluted Mexican environments.

The observations of larger-than-normal  $\text{NO}_x$  and HCN emissions from the MC-area fires may also be relevant to understanding the local-regional atmospheric chemistry in other fire-impacted urban areas such as the Los Angeles basin where Radke et al. (1991) observed fire-induced resuspension of CFC-12. In addition, Hegg et al. (1987) measured higher emissions of  $\text{NO}_x$ ,  $\text{SO}_2$ , and particle nitrate from burn-

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ing chaparral near Los Angeles than in the Pacific Northwest. In the latter study, the fuel types were different and the higher emissions of flaming compounds from chaparral were very likely partly due to the higher MCE of the chaparral fires, but deposition/resuspension probably also contributed to the difference as they suggested. In our study, we seem to support their hypothesis in a comparison of more similar fuel types. If industrial deposition does impact fire emissions, this could also be important in the southeastern US where widespread prescribed burning occurs near urban areas and in most urban areas in “developing countries” which usually coexist with biomass burning.

### 3.4 Overview of particle chemistry

TEM studies show that many of the aerosol particles consist of internally mixed aggregates of several distinct particle types. For example, Figure 5 shows a range of such particles ( $<0.3\mu\text{m}$  aerodynamic diameter) together with their compositions, measured using energy dispersive X-ray spectrometry (EDS). This sample was collected when the Twin Otter passed through the plume of the planned fire on 17 March. Identified particle types include soot, clay (probably kaolinite), tar balls, other organic material (OM), and a variety of sulfates and nitrates with and without K. The ammonium sulfates as well as  $\text{KNO}_3$  and, to a lesser extent,  $\text{K}_2\text{SO}_4$  tend to decompose in the electron beam and are thus difficult to analyze using TEM. Some OM particles have inclusions of K compounds like the products of biomass burning from other areas, although we did not observe discrete crystals of KCl like those found during SAFARI-2000 (Pósfai et al., 2003; Li et al., 2003). The inclusions of K compounds appear darker than their host OM (Fig. 5a) (Pósfai et al., 2003). The tar balls are round, amorphous OM particles that occur as a result of biomass burning (Pósfai et al., 2004, Hand et al., 2005). Although EDS analysis is not sensitive for detecting light elements such as N, most OM particles clearly showed a N peak (Figs. 5c and d). The OM particles without identifiable inclusions of K compounds and ammonium sulfate such as particle OM (3) (Figs. 5a and c) also contained N. As burning of pine forests in the MC area emits large amounts of

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NO<sub>x</sub> (see Sect. 3.3), the gaseous nitrogen may also contribute to the N in OM particles and, conversely, particles may host an appreciable fraction of the emitted N.

### 3.5 Preliminary assessment of the contribution of fires to the MC plume

Fire emission factors can be multiplied by fuel consumption data to estimate total emissions at various scales. However, it is difficult to measure the amount of fuel burned for a large geographic fire-prone area. Consideration of the fires we sampled, combined with the MODIS hotspots, allows a crude estimate of the total fuel burned by mountain fires in the study area during March 2006. We base our rough estimate on the assumption that the planned fire had a size (22.2 ha), duration (~1 h) and fuel consumption (6.54 Mg/ha) that is approximately average for the study area mountain fires. These assumptions seem conservative since the total fuel consumption of 145 Mg was about one-half the average total fuel consumption of 295 Mg for the 5 fires sampled by the ground crew in the area. We approximate the time period during which “average fires” burn as noon to five PM local time. (We choose noon as the beginning of the burning period because during one flight to southern Mexico we actually observed numerous fires being simultaneously ignited over a large, previously-clean area a few minutes after noon.) We note that cloud-free MODIS coverage of the study area (98–100 W and 19–20 N) during this “burning period” occurred on 2 of the 4 days (or one-half of the days) that the Twin Otter sampled fires there. If the average fire lasts for one hour, then an overpass during the burning period could detect up to one-fifth of the average fires if they were evenly distributed throughout the burning period. Coupling the above factors suggests that the actual number of mountain fires could be about 10 times larger than the 218 detected from space. Thus, 2180 fires times the total fuel consumption for the planned fire (145 Mg) estimates the total fuel consumption by these fires for the study area for March 2006, which is ~317 000 000 kg.

If the average fire duration is actually longer than the 1 h duration of the planned fire or if the number of fires peaks sharply at overpass time, then we have overestimated the number of fires, but this error could tend to be cancelled by the larger total fuel

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consumption expected for longer-lasting or more intense (mid-afternoon) fires. (The key assumption is the fuel consumption rate.) The study-area fuel consumption estimated this way may well be a lower limit since it does not include fires that are too small to register as hot spots (but potentially numerous) or large multi-day fires that would consume fuel for more than 5 h per day (several were observed from the Twin Otter in restricted airspace and one was measured at ~300 ha by the ground crew). A good, satellite-based, burned area measurement for this region would reduce the uncertainties associated with our assumptions above, but is not available to our knowledge. This estimate also explicitly leaves out any small-scale urban burning for cooking, garbage disposal, etc.

In any case, the study-area fuel consumption times the EF in Table 2 gives an estimate of the total, study-area, mountain fire emissions of each species for the month. Our total mountain-fire CO emissions can be compared to 1/12 of the annual CO in the MC metropolitan area emissions inventory (MCMAEI) (West et al., 2004) and they represent about 18 % of that value. Thus this analysis implies that these fires were responsible for about 15% of the CO exported in the March 2006 MC-area plume, although West et al. argued that the CO and VOC emissions may be underestimated in the MCMAEI. Our preliminary, bottom-up estimate suggests similar fire contributions to the total for NO<sub>x</sub> (12 %) and VOC (14%) and coincidentally the NO<sub>x</sub>/VOC ratio from fires (~0.38) is similar to that in the MCMAEI (~0.43). In contrast to the similar contributions calculated for the trace gases above, the fire contribution to the PM is estimated to be much larger at 68%. The true contribution could be higher since PM<sub>1</sub>/PM<sub>10</sub> from fires is about 0.7 (Andreae and Merlet, 2001). (The MCMAEI tabulates PM only as PM<sub>10</sub>.) The above estimates also do not include the fire emissions due to residual smoldering combustion in the mountains, MCMA cooking/garbage fires, or any other biomass burning, which cannot be sampled from an aircraft (Bertschi et al., 2003a, b; Yevich and Logan 2003). Another relevant insight is derived by noting that the PM<sub>10</sub>/CO mass ratio in the MCMAEI is ~0.011, whereas the PM<sub>1</sub>/CO ratio from mountain fires was ~0.133. Thus, regardless of the fire contribution to the MC-area plume CO, the

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fire contribution to PM should be much greater. No upward adjustment of the MC PM emissions was indicated by the modeling efforts of West et al. (2004). Thus, the fire emissions almost surely make their largest contribution to the MC-area plume, on a mass basis, via particle loading.

5 The contribution of fire emissions to the MC-area plume can be estimated by another approach since HCN and CH<sub>3</sub>CN are both thought to be emitted primarily by biomass burning (Li et al., 2000; de Gouw et al., 2006). For example, our fire ER HCN/CO can be coupled with regional measurements of HCN/CO in ambient air to estimate the biomass burning contribution to regional CO. This analysis rests on the assumption  
10 that the study-average mix of fire emissions we sampled resembled the real, average fire-emissions mix – on the days of the downwind measurements – and it requires that other types of burning that may occur in the study area are ignored. The unusually high HCN emissions we observed are also important to incorporate in this type of analysis.

Explicitly, the average MC-area mountain fire ER for HCN/CO measured on the Twin  
15 Otter is  $\sim 0.0128 \pm 0.0096$  on a molar basis. The single MC-area fire measurement of HCN/CO on the C-130 was 0.011, which is in good agreement with the Twin Otter mean. The average downwind regional HCN/CO molar ratio measured on the C-130 in ambient air is about  $0.003 \pm 0.0003$  implying that about 23% of the study area CO was from the mountain fires we sampled. This is actually fairly consistent with our  
20 crude bottom-up estimate above. Note, that use of fire HCN/CO ER from the other sources shown in Fig. 4 would have increased the estimate of the biomass burning contribution by a factor of 2–9. Of course, due to the large uncertainty regarding both urban and fire emissions mentioned above, it would be preferable to average estimates based on as many different biomass burning indicators as possible (e.g. HCN, CH<sub>3</sub>CN,  
25 CH<sub>3</sub>Cl, particle <sup>14</sup>C, etc. . . ). We can go a step further with the “tracer-based analysis” since according to the fire and urban PM/CO ratios quoted above; a 23% fire contribution to study-area CO implies a 78% contribution to PM. This again makes fires the main source of PM in the (March 2006) MC-area plume. Finally we note that both the bottom-up estimate and the “tracer-based analysis” leave open the possibility that other

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types of burning in the study area (cooking, garbage burning, etc. . . ) make substantial additional contributions to the total MC-area outflow.

5 In addition to the near-source mixing of fire and urban emissions in the MC-area plume, we note that the more aged MC-area plume also likely interacts with biomass burning emissions from other regions of Mexico. For example, on 12 March and 29 March the Twin Otter sampled (mostly) widespread agricultural waste burning (also characterized by relatively high N emissions) on the western Yucatan peninsula. On both of these days, HYSPLIT forward trajectories from our western Yucatan fires trend to the NW and pass close to the NE-trending forward trajectories from MCMA over the  
10 Gulf of Mexico (Draxler and Rolph, 2003). The projected possible mixing would be after emissions from both sources had aged 1–3 days. To aid in modeling this potential interaction, the Twin Otter sampled approximately 20 fires on the Yucatan and the C-130 also sampled 2 fires there. The results for those fires will be presented separately.

### 3.6 Possible nature of fire impacts on the MC-area plume photochemistry

15 The main purpose of this paper is to present the study area EF and a preliminary assessment of their significance. Having established that fires will likely produce a visible signal in the MC-area plume measurements we now just list some fairly obvious potential influences of fires on the plume photochemistry. Introductory material about these affects can be found in atmospheric chemistry textbooks (Finlayson-Pitts and  
20 Pitts, 1986). For example, the injection of fresh “fire- $\text{NO}_x$ ” into the MC plume immediately downwind of MC could contribute to the measured change in the  $\text{NO}_x/\text{NO}_y$  ratio between downtown MC and further downwind. Both  $\text{NO}_x$  and VOC from fires could alter the downwind  $\text{O}_3$  production (which could also be impacted by the high dust levels observed).  $\text{NO}_x$  from fires could also contribute to aerosol nitrate (Fig. 5). Ammonia is  
25 another reactive fire emission that could contribute to aerosol particles such as ammonium sulfate or ammonium bisulfate and affect secondary aerosol formation in general. The particles emitted by fires are enriched in organic carbon (Fig. 5a) compared to particles from industrial sources and this could affect observed downwind heterogeneous

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chemistry. Also, the addition of organic rich particles to the MC plume by fires should not be confused with secondary aerosol formation. Confirmation of any of these, or other, impacts may be found in the MILAGRO airborne data.

3.7 Relevance to earlier measurements in Mexico City urban area

5 Previous atmospheric chemistry measurements in the MC-area were nearly all ground-level measurements in the heart of the MC urban area. An influence of biomass burning was recognized in some of these reports. Bravo et al. (2002) analyzed the particulate data for the MC urban area from 1992 to 1999. They observed some large increases in urban PM10 and TSP during March-May of 1998, which they attributed to greatly  
10 increased biomass burning in Mexico at that time (Galindo et al., 2003). Moya et al. (2003) analyzed urban MC particulate from December 2000 to October 2001. There was a marked peak in total loading during April of 2001, which coincides with the usual annual peak of fire activity in the area.

A number of researchers in the MCMA-2003 campaign noted a biomass burning  
15 influence on the April 2003 urban particle data as reported by Molina et al. (2007). In particular, Johnson et al. (2006) estimated that on average, for April 2003, biomass burning contributed about 12% of the particle mass (their Fig. 1). However, there are some intriguing aspects of their data worth noting. For instance, K, H, and Cl, which are said to be elemental markers of biomass burning, increased strongly in the 0.07–  
20 0.34 and 1.15–2.5 micron size ranges late in the month when fire activity increased (their Fig. 4). However, in the 0.34–1.15 micron size range, which accounts for most of the mass of biomass burning particles, the increase was much smaller. In any case, we note that a 12% contribution of fires to ground-level downtown MC PM is not a-priori incompatible with our estimate of fires producing 70–80% of the PM in the  
25 study area. For any given wind direction, emissions from the fires in at least half the area (downwind and parallel) would not be expected to find their way to downtown MC. Even for directly upwind mountain fires, much of the emissions could pass above ground-level monitors.

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## 4 Conclusions

The MILAGRO experiment was conducted to further the understanding of the outflow from the MC area. This paper presents data that is useful for modeling the biomass burning contribution to the outflow photochemistry. The average fire emissions of HCN were  $\sim 2$  times higher than normally observed for biomass burning, which should be taken into account in source apportionment. The average fire emissions of  $\text{NO}_x$  were 2–4 times higher than would be assumed based on literature values. This is important in modeling plume photochemistry. The high N emissions from MC-area fires may be relevant to understanding atmospheric chemistry throughout the world in the many urban areas that coexist with biomass burning. Preliminary analysis suggests that fires produce about 12–23% of the CO, VOC, and  $\text{NO}_x$  in the plume leaving the MC-area, but a much larger percentage ( $\sim 68$ –78%) of the particles. Thus, the particle contribution to the MC-area plume is likely the most important fire contribution and fires may be the main source of particles in the Mexico City area outflow.

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**Table 1.** Locations, times, and fuel consumption for the pine-savanna fires sampled by MILA-GRO aircraft or ground crew in mountains surrounding Mexico City.

| Fire Name                      | Sampled by         | Burn Date(s)<br>dd/mm/yyyy | Lat (N)<br>dd.dddd | Long (W)<br>dd.dddd | time of airborne sampling |                         | Coverage by cloud-free MODIS OP               |       |                | UMD hotspot?<br>Y or N | Fuel tion<br>Mg total | Consump-<br>tion<br>hectares |
|--------------------------------|--------------------|----------------------------|--------------------|---------------------|---------------------------|-------------------------|---|-------|----------------|------------------------|-----------------------|------------------------------|
|                                |                    |                            |                    |                     | start<br>hh:mm<br>(LT)    | finish<br>hh:mm<br>(LT) | Terra<br>(LT)                                 | hhmm  | Aqua hhmm (LT) |                        |                       |                              |
| 3.6-F1                         | To <sup>a</sup>    | 06/03/2006                 | 19.0763            | 99.0537             |                           | 13:27                   | 11:15   | 14:20 | N              |                        | nm                    | nm                           |
| 3.6-F2                         | TO, G <sup>b</sup> | 06/03/2006                 | 19.1739            | 99.1903             |                           | 13:32                   | 11:15   | 14:20 | N              |                        | 61                    | 7.7                          |
| 3.6-F3                         | TO                 | 06/03/2006                 | 19.1881            | 99.3783             | 17:05                     | 17:09                   | 11:15   | 14:20 | N              |                        | nm                    | nm                           |
| 3.6-F4                         | TO                 | 06/03/2006                 | 19.0711            | 99.2283             |                           | 17:14                   | 11:15   | 14:20 | N              |                        | nm                    | nm                           |
| M6 F12                         | G                  | 06/03/2006                 | 19.3142            | 99.4290             |                           | none                    | 11:15   | 14:20 | N              |                        | 85                    | 3.7                          |
| 3.9-F1                         | TO                 | 09/03/2006                 | 19.3269            | 99.4775             |                           | 13:20                   | 11:41   | none  | N              |                        | nm                    | nm                           |
| 3.10-F1                        | C-130              | 10/03/2006                 | 19.6431            | 98.3578             |                           | 17:16                   | 10:55   | 13:55 | N              |                        | nm                    | nm                           |
| 3.17-PF                        | TO, G              | 17/03/2006                 | 19.0681            | 99.0616             | 11:58                     | 12:42                   | 10:55   | 14:00 | N              |                        | 145                   | 22.2                         |
| 3.17-F2                        | TO                 | 17/03/2006                 | 19.3862            | 98.6066             | 13:06                     | 13:18                   | 10:55   | 14:00 | N              |                        | nm                    | nm                           |
| 3.18-F2                        | TO, G              | 18/03/2006                 | 19.3456            | 98.6851             | 15:46                     | 16:39                   | 11:34   | none  | N              |                        | 873                   | 27.2                         |
| 3.18-F3                        | G                  | ~17–<br>19/03/2006         | 19.3174            | 98.6888             |                           | none                    | Hotspot at 19.32, –98.72 (3/17 AQUA at 14:00) |       |                |                        | ~3100                 | ~300                         |
| M6 F8                          | G                  | unknown                    | 19.2252            | 99.3934             |                           | none                    |   |       | N              |                        | nm                    | 6.9                          |
| Approximate Mexico City Center |                    |                            | 19.411             | 99.131              |                           |                         |   |       |                |                        |                       |                              |

<sup>a</sup> TO indicates USFS Twin Otter (see text).

<sup>b</sup> G indicates ground-based fire characterization crew (see text).

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**Table 2.** Emission Factors for the Pine-Savanna Fires Sampled in the Mountains Surrounding Mexico City in March 2006.

| Species                       | 6 March<br>Fires 1–4<br>EF (g/kg) | 9 March<br>Fire 1<br>EF (g/kg) | 17 March<br>Planned Fire<br>EF (g/kg) | 17 March<br>Fire 2<br>EF (g/kg) | 18 March<br>Fire 2<br>EF (g/kg) | All Fires<br>Average | All Fires<br>Standard Deviation |
|-------------------------------|-----------------------------------|--------------------------------|---------------------------------------|---------------------------------|---------------------------------|----------------------|---------------------------------|
| CO <sub>2</sub>               | 1655                              | 1652                           | 1747                                  | 1611                            | 1646                            | 1662                 | 51                              |
| CO                            | 83.2                              | 88.6                           | 30.9                                  | 112.5                           | 99.2                            | 82.9                 | 31.1                            |
| MCE                           | 0.927                             | 0.922                          | 0.973                                 | 0.901                           | 0.914                           | 0.927                | 0.027                           |
| NO                            | 6.14                              | 5.88                           | 1.95                                  | 2.68                            |                                 | 4.16                 | 2.16                            |
| NO <sub>2</sub>               | 5.51                              | 6.70                           | 3.37                                  | 4.54                            |                                 | 5.03                 | 1.42                            |
| NO <sub>x</sub> as NO         | 9.73                              | 10.25                          | 4.15                                  | 5.64                            |                                 | 7.44                 | 3.01                            |
| H <sub>2</sub>                | nm                                | nm                             | nm                                    | nm                              | 1.51                            | 1.51                 | nm                              |
| CH <sub>4</sub>               | 6.92                              | 5.00                           | 2.81                                  | 4.69                            | 5.39                            | 4.96                 | 1.48                            |
| C <sub>2</sub> H <sub>4</sub> | 0.90                              | 0.36                           | 1.38                                  | 1.17                            | 0.88                            | 0.94                 | 0.38                            |
| C <sub>2</sub> H <sub>2</sub> | 0.24                              | nm                             | 0.20                                  | 0.12                            | nm                              | 0.19                 | 0.06                            |
| C <sub>2</sub> H <sub>6</sub> | 0.34                              | nm                             | 0.35                                  | 0.55                            | 1.09                            | 0.58                 | 0.35                            |
| C <sub>3</sub> H <sub>6</sub> | 0.19                              | nm                             | 0.42                                  | 0.48                            | 0.92                            | 0.50                 | 0.30                            |
| HCHO                          | 2.37                              | 3.32                           | 3.73                                  | 2.55                            |                                 | 2.99                 | 0.64                            |
| CH <sub>3</sub> OH            | 1.48                              | 2.56                           | 1.45                                  | 2.77                            |                                 | 2.06                 | 0.70                            |
| CH <sub>3</sub> COOH          | 3.18                              | 6.65                           | 3.61                                  | 2.40                            |                                 | 3.96                 | 1.86                            |
| HCOOH                         | 1.66                              | 4.34                           | 1.83                                  | nm                              |                                 | 2.61                 | 1.50                            |
| NH <sub>3</sub>               | 1.81                              | 0.65                           | 0.30                                  | 0.89                            |                                 | 0.91                 | 0.65                            |
| HCN                           | 1.50                              | 0.32                           | 1.67                                  | 0.60                            |                                 | 1.02                 | 0.66                            |
| propane                       | 0.948                             | nm                             | 0.141                                 | 0.069                           |                                 | 0.386                | 0.488                           |
| isobutane                     | 0.119                             | nm                             | 0.015                                 | nm                              |                                 | 0.067                | 0.074                           |
| n-butane                      | 0.326                             | nm                             | 0.040                                 | nm                              |                                 | 0.183                | 0.202                           |
| t-2 butene                    | 0.013                             | nm                             | 0.030                                 | 0.044                           |                                 | 0.029                | 0.016                           |
| 1-butene                      | 0.042                             | nm                             | 0.086                                 | 0.105                           |                                 | 0.078                | 0.032                           |
| isobutene                     | 0.053                             | nm                             | 0.072                                 | 0.118                           |                                 | 0.081                | 0.033                           |
| c-2-butene                    | 0.010                             | nm                             | 0.021                                 | 0.031                           |                                 | 0.021                | 0.011                           |
| cyclopentane                  | 0.004                             | nm                             | 0.002                                 | nm                              |                                 | 0.003                | 0.001                           |
| isopentane                    | 0.032                             | nm                             | 0.011                                 | nm                              |                                 | 0.022                | 0.015                           |
| n-pentane                     | 0.051                             | nm                             | 0.018                                 | 0.008                           |                                 | 0.026                | 0.023                           |
| 1,3 butadiene                 | 0.042                             | nm                             | 0.090                                 | 0.069                           |                                 | 0.067                | 0.024                           |
| PM <sub>1</sub>               | 7.08                              | 7.40                           | 6.83                                  | 21.0                            | 13.0                            | 11.05                | 6.10                            |

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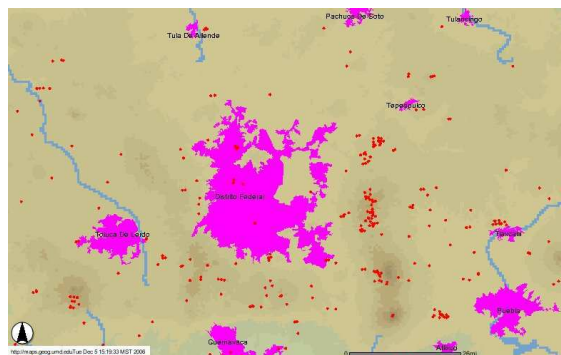
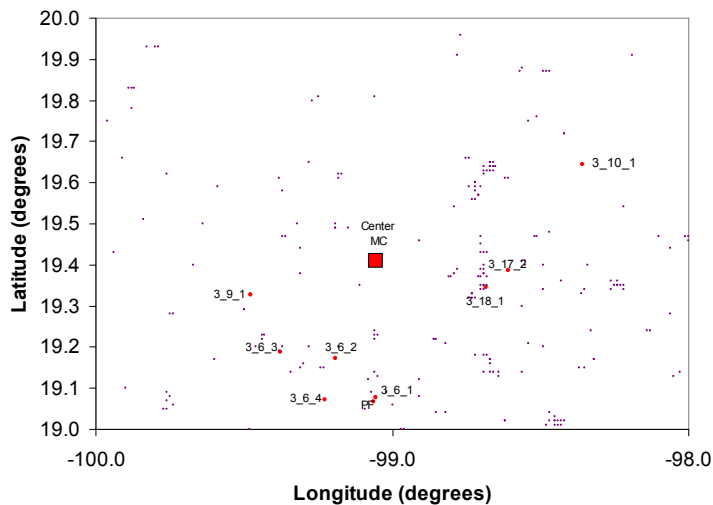
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**Fig. 1. (a)** The locations of the pine-forest fires sampled in the mountains surrounding Mexico City are shown with large red dots. MODIS hotspots detected during March 2006 in the same geographic area are shown as smaller purple dots. **(b)** The MODIS hotspots shown in relation to urban areas.



**Fig. 2.** Photo taken a few km northwest of the site of fire 3.6\_4 on 6 March at 05:13 p.m. local time. A large number of pine-forest fires are burning in, and mixing with, the MC outflow on a mountain pass to the south of the city.

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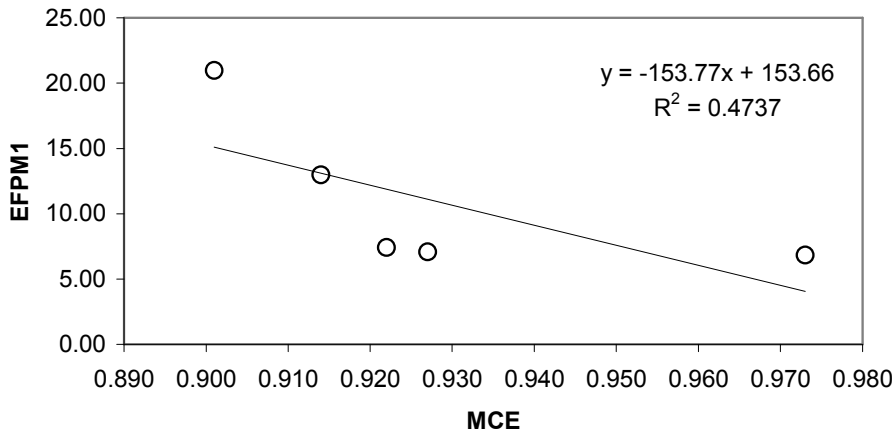
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**Fig. 3.** Fire-average emission factors (EF) plotted versus fire-average modified combustion efficiency (MCE) for PM1 (data from Table 2). A range of EF occurs, which correlates with the relative amount of flaming and smoldering.

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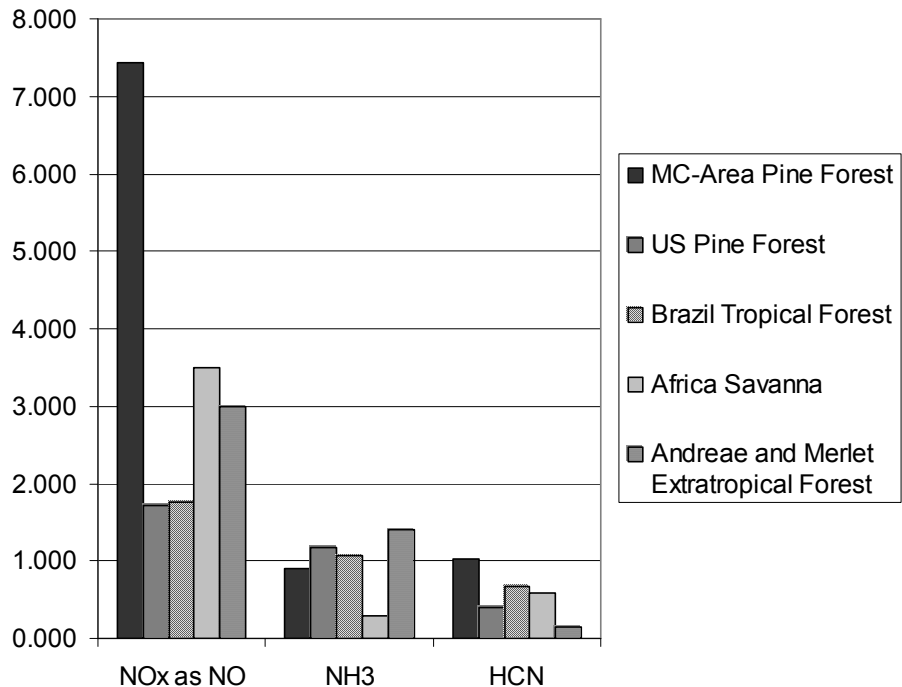
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**Fig. 4.** Comparison of EF for selected nitrogen containing species between the MC-Area pine forest, tropical forest in Brazil, and savanna in Africa.

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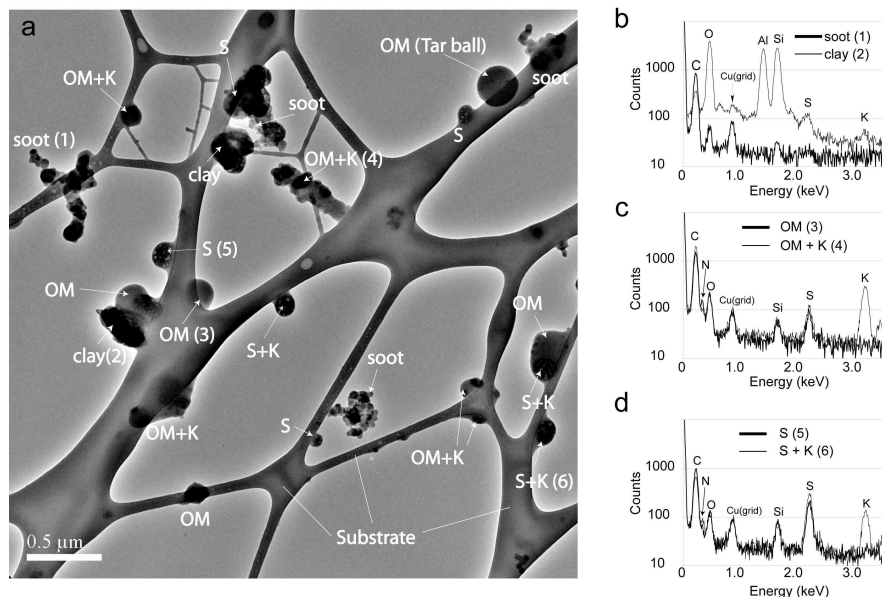
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**Fig. 5.** Bright-field TEM image and EDS spectra of particles collected approximately 40 km south of the center of MC (sample 3.17-PF in Table 1 and Fig. 1a; collected 17 March 2006; start time 11:57:50, stop time 11:58:30 – local time,). They are the products of biomass burning (forest fire). **(a)** Image of various kinds of particles on a substrate of lacey carbon. OM — organic material, OM + K — organic material with inclusions of K compounds, S — sulfate, and S + K — ammonium and K sulfate. **(b)** EDS spectra for the particles in Fig. (a). The particle types were identified by their compositions and morphological properties. Numbers (1) to (6) in the inserts in Figs. (b) to **(d)** correspond to particles in the TEM image (Fig. a). The Cu peaks in the spectra are from the TEM grids.

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